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Determination of ^{129}I in seawater and some environmental materials by neutron activation analysis

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A neutron activation analysis method with pre-irradiation separation and post-irradiation purification is presented for the determination of ^{129}I content and ^{129}I/^{127}I ratio in some environmental samples, such as seawater, seaweed, grass and soil. An evaporation concentration followed by solvent extraction was used for the separation of iodine from seawater, and alkaline ashing or alkaline fusion followed by water leaching and solvent extraction for vegetation and soil samples. A further post-irradiation purification of iodine was carried out by extraction and PdI_2 precipitation. The concentrations of ^{129}I and ^{127}I were then measured by counting ^{130}I and ^{126}I, respectively. The recoveries of iodine reach 60–95% and more than 98% in pre-concentration and post-irradiation purification procedures, respectively. The detection limit of this method for ^{129}I reached $2–3 \times 10^{-13}$ g. Some samples collected in Denmark and Iceland were analysed.

Iodine-129 is the only naturally occurring radioisotope of iodine with a long half-life of 1.57×10^7 a. Although all ^{129}I formed in the primordial nucleosynthesis has decayed to ^{129}Xe, and only one stable isotope of iodine, ^{127}I, remains in the Earth, natural processes, such as spontaneous fission of ^{238}U, thermal neutron-induced fission of ^{235}U and spallation reactions of Xe in the upper atmosphere contribute to a steady state concentration of ^{129}I. The estimated atom ratio of ^{129}I/^{127}I in the marine environment is between 3×10^{-13} and 3×10^{-12} and 10^{-15}–10^{-14} in the lithosphere.[1]

Since 1945, the atom ratio of ^{129}I/^{127}I in the environment has been significantly increasing by nuclear weapon tests as well as the peaceful use of nuclear energy. The cumulative global release of ^{129}I due to nuclear weapons testing has been estimated to be 57 kg,[1] and the ratio of ^{129}I/^{127}I in the marine environment was increased to 10^{-11}–2×10^{-10} and 10^{-9}–10^{-7} in the terrestrial environment. However, the largest source of anthropogenic ^{129}I in the environment by far is the reprocessing of spent nuclear fuel. Recently, it was estimated that some 1400 kg of ^{129}I was discharged by two main reprocessing plants at Sellafield, UK and Cap de La Hague, France over the past three decades.[2–4] Such large discharges of ^{129}I to the ocean make it a unique tracer for the study of the movement of water masses, transfer of radionuclides and marine cycles of stable non-conservation elements such as iodine and carbon. In fact, using ^{129}I as an environmental tracer was discussed as early as 1962.[5,6] However, until recently, this potential was exploited using reprocessing discharged ^{129}I.[3, 7–11]

Because iodine is an essential trace element for humans and is highly concentrated by the thyroid, the transfer of radioiodine to humans is a more important problem, which should be extensively studied. The determination of ^{129}I in environmental and human samples can be used not only for evaluation of exposure of humans to ^{129}I radiation, but also to re-construct the past level of more dangerous short-lived radioiodine isotopes ^{131}I and ^{133}I, and evaluate the exposure of humans to it and its transfer pathways.[12,13]

Much attention has been focused on the environmental level of ^{129}I and the pathways linking radioiodine deposition in the environment and its transfer to the food chain *via* soil–grass–milk–human.[14–24] But up to now, no ^{129}I data have been reported in the environment of Denmark, which experiences the influence of radioactive discharges and fallout from many sources.

Many methods can be used for the determination of ^{129}I, but for ^{129}I at environmental levels, only neutron activation analysis (NAA) and accelerator mass spectrometry (AMS) can be used, in which AMS is the most sensitive method available today. But, because a high-energy accelerator is needed for this method, it is not commonly available. As a consequence, NAA is first and most often used for the analysis of ^{129}I. In this work, NAA with pre-irradiation separation and post-irradiation purification was developed for the determination of ^{129}I in seawater, seaweed, soil and grass samples collected in Denmark.

Many determinations of ^{129}I in fresh water have been reported (see later) but little work has been reported on the analysis of seawater,[3,7–10] and none was carried out by NAA. The reason is probably the much lower ^{129}I concentration in normal seawater (10^{-12}–10^{-9} for ratio of ^{129}I/^{127}I) and difficulties in the separation and pre-concentration of enough iodine from seawater. Seawater, unlike fresh water, contains a large number of inorganic ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and Br^-, and this makes the separation of iodine more difficult. In the analysis of total iodine in seawater, ion-exchange and extraction were usually used for the separation of iodine from a small amount of seawater. Zhou[8] separated iodine from less than 0.9 l seawater for the determination of ^{129}I by AMS. However, it cannot be directly used for neutron activation analysis of seawater with a ratio of ^{129}I/^{127}I less than 10^{-7}. In this work, a pre-concentration method of iodine from a large volume of seawater for the determination of ^{129}I by NAA is presented.

1 Experimental

1.1 Samples and chemicals

Brown algae *Fucus vesiculosus* were collected in Klint, Denmark and Iceland, and dried at 105 °C before storage. Seawater was collected in Roskilde Fjord, Denmark. Before analysis, it was filtered through a filter paper. Grass was collected in Risø of Roskilde and Valby, Denmark. It was dried at 70 °C for about 48 h, then ground into small pieces. Surface soil sample (0–5 cm) was collected in Risø of Roskilde, Denmark. It was dried at 70 °C for about 48 h, and ground. The sampling sites of grass, soil, seawater and some seaweed are shown in Fig. 1.

The standard solution of ^{129}I (NIST-SRM-4949c) was purchased from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. Carrier free ^{125}I and ^{131}I solutions were purchased from Amersham Pharmacia Biotech, Little Chalfont, Buckinghamshire, UK. Other chemical reagents used were of analytical reagent grade.

1.2 Pre-concentration of iodine

1.2.1 Vegetation samples (seaweed and grass). Dried seaweed or grass (40 g) was placed in a crucible; 160 ml KOH (1.0 mol l^{-1}) and 0.2 ml ^{125}I (100 Bq) solution for measurement of chemical yield were added. After the sample was completely mixed, the crucible was placed in an oven to dry at 70–80 °C for about 35–40 h. The dried samples were moved to a muffle furnace, and firstly heated at 350 °C for 1 h to burn, and then ashed at 650 °C for 4 h. After cooling, iodine was leached with hot deionized water, filtering to remove the unashed residue. Adding 2 ml of $KHSO_3$ (0.3 mol l^{-1}) for prevention of oxidation of iodide to molecular iodine, the leachate was acidified to pH 1–0.5 with HNO_3 with stirring, the acidified leachate was transferred to a separation funnel, shaking to completely release all gas produced by acidification. CCl_4 and 0.4 ml of $NaNO_2$ (0.5 mol l^{-1}) were added to the funnel, with shaking to extract iodine into the CCl_4 phase as elemental iodine. The extraction procedure was repeated, the organic phases were combined and iodine was back-extracted with 10–20 ml H_2SO_3 solution (0.02 mol l^{-1}). This extraction and back-extraction procedure were repeated twice.

LiOH (0.3%) solution and MgO powder were then added to the back-extracted aqueous phase to adjust the pH to 8–9 (less than 2 ml LiOH solution). The solution was carefully evaporated to $\approx$0.5 ml on a hotplate and then transferred to a quartz ampoule (10 mm diameter and 50 mm length), after which it was dried at 70–80 °C. The recovery of iodine in the pre-irradiation chemical separation was determined by the measurement of ^{125}I with a HeGe detector, which is the same as that for the measurement of ^{130}I and ^{126}I.

1.2.2 Soil sample. Taking 3–5 g soil to a crucible, 10 g KOH, 0.2 ml ^{125}I solution (100 Bq) and 3.0–4.0 ml water were added. After the sample was completely mixed, the crucible was placed in an oven to dry at 70–80 °C for about 48 h. The dried samples were heated gradually to 600 °C and maintained at this temperature for 2 h in a muffle furnace to burn and fuse the sample. After cooling, iodine was leached with hot deionized water. After adding 2 ml of $KHSO_3$ (0.3 mol l^{-1}), leachate was acidified to pH 1–0.5 with concentrated HNO_3 with stirring, followed by centrifugation to remove residues. Thereafter the iodine was separated and concentrated by the extraction and back-extraction cycle described in the above section.

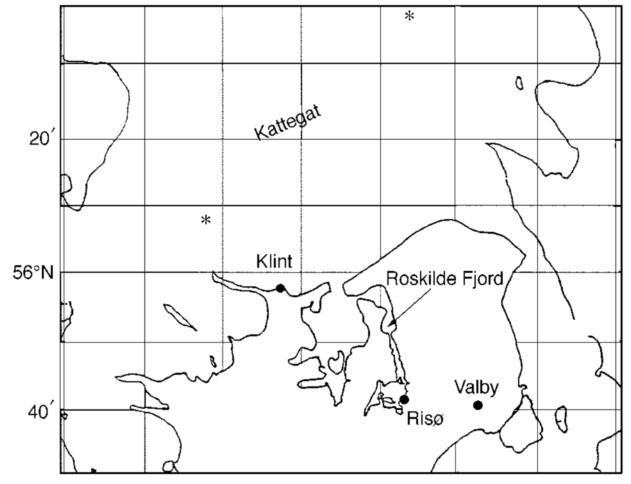

Fig. 1 Distribution of the sampling location in Denmark (* sampling location by Zhou, ● sampling location in this work).

1.2.3 Seawater samples. Taking 4–10 l filtered seawater to a beaker, 2 ml of 0.3 mol l^{-1} $KHSO_3$, 1-2 mg iodine (KI), 0.2 ml ^{125}I solution (100 Bq) and 15-20 ml KOH (1.0 mol l^{-1}) solution were added, after which the sample was evaporated on a hotplate to 0.4–1 l. The concentrated seawater was filtered through a filter paper. Concentrated HNO_3 and 2.0 ml of $KHSO_3$ (0.3 mol l^{-1}) were added to acidify the seawater to pH 1 and convert different forms of iodine to iodide. The iodine in the leachate was then separated by the method described in section 1.2.1.

1.3 Preparation of ^{129}I standard

One ml of ^{129}I solution (^{129}I: 2.24 $\times$ 10^{-8} g ml^{-1}; ^{127}I: 0.404 mg ml^{-1}), which was prepared by dilution of an original standard solution (NIST-SRM-4949c), was added to 25 ml H_2O with 505.4 mg iodine (KI). The iodine (^{129}I and ^{127}I) was separated by the extraction and back-extraction cycle described in section 1.2.1. The back-extracted aqueous phase was neutralized to pH $>$8.0 with LiOH solution, and the volume was adjusted to 50 ml with deionized water. This solution, containing 4.48 $\times$ 10^{-10} g ^{129}I ml^{-1} and 10.12 mg ^{127}I ml^{-1} (the ratio of ^{129}I/^{127}I is 4.43 $\times$ 10^{-8}), was used as ^{129}I and ^{127}I comparative standard solution.

A portion (0.4 ml) of the above ^{129}I standard solution was added to a quartz ampoule, and dried at 70–80 °C. The contents of ^{129}I and ^{127}I in this ^{129}I comparative standard were 1.76 $\times$ 10^{-10} g and 4.05 mg, respectively.

1.4 Neutron activation analysis

Sealed sample and standard ampoules were irradiated at a thermal neutron flux of 4.0 $\times$ 10^{13} n cm^{-2} s^{-1} for 10 h in a Danish DR-3 reactor.

1.5 Post-irradiation purification of iodine

After 10–15 h decay, the quartz ampoule was broken under a solution containing 30 ml of deionized water, 2 ml of 0.3 mol l^{-1} $KHSO_3$, 10 mg Br^- and 20 mg I^- in a beaker. 3 ml of 1.0 mol l^{-1} HNO_3 was then added to the beaker to dissolve the irradiated sample. Iodine was purified by three cycles of extraction with CCl_4 and back-extraction with $KHSO_3$ solution.

A portion (2–5 ml) of $PdCl_2$ solution (15 mg Pd^{2+} ml^{-1}) was added into the back-extracted aqueous phase; the precipitated iodine as PdI_2 was separated by filtering through a Millipore filter. The precipitate with filter was sealed in a polyvial for measurement.

1.6 Measurement of ^{130}I and ^{126}I

The ^{130}I and ^{126}I, which were produced from ^{129}I and ^{127}I by neutron irradiation, were measured for 1–10 h using a HpGe detector, coupled to a Canberra 8000-channel analyser. This system has a resolution of 1.89 keV at 1332 keV and a relative efficiency of 35%. The γ-rays of 536 keV and 388.5 keV of ^{130}I and ^{126}I were used to calculate the activities of these two nuclides, respectively. The contents of ^{129}I and ^{127}I were calculated by a relative method by comparing with a ^{129}I standard.

1.7 Determination of ^{127}I in grass, seawater and soil samples

The concentrations of stable iodine (^{127}I) in some samples were determined by measuring ^{128}I produced by the reaction ^{127}I(n, γ)^{128}I. The analytical methods for grass and seawater have been described in detail elsewhere.[25,26] For soil samples, 0.5 ml of separated iodine solution (see section 1.2.2) was taken and sealed in a half-dram polyvial. The iodine content was determined by radiochemical NAA.[25]

2 Results and discussion

Table 1 shows the analytical results of ^{129}I and ^{127}I and calculated ratios of ^{129}I/^{127}I in seaweed, seawater, grass and soil samples. It can be observed that the samples with a ratio of ^{129}I/^{127}I as low as 4×10^{-10} can be determined with a measurement uncertainty less than 7%, and for grass and soil samples, ^{129}I as low as 10^{-12} g can be determined with an error less than 20%.

Zhou[8] and Yiou *et al.*[7] determined the ^{129}I concentrations and ^{129}I/^{127}I ratios in some seawater and seaweed samples collected from Kattegat (Fig. 1) and Iceland by AMS. They observed that the ratio of ^{129}I/^{127}I in seawater from Kattegat in 1992 ranged from 3.26–6.19 $\times 10^{-8}$, and 2.4–3.9 $\times 10^{-10}$ in seaweed from Iceland in 1990–1991. Our results in Klint, which is close to their sampling site in Kattegat (Fig. 1), and Iceland are in good agreement with theirs.

The sampling sites of soil and grass in Roskilde and seawater in Roskilde Fjord are located near Risø National Laboratory, at which soil and grass samples were collected at the same site. These two sampling sites are just about 300 m from the Danish DR-3 reactor and closed DR-2 reactor. Other grass samples were collected from Valby, 30 km from Risø. From Table 1, no difference can be seen in the concentration of ^{129}I in grass samples collected from Risø and Valby. The ratio of ^{129}I/^{127}I in grass from Valby is higher than that from Risø because of two-times lower stable iodine concentrations in grass from Valby than that from Risø. This may be explained by just about 300 m distance from the grass sampling site in Risø to the coast of Roskilde Fjord. This result indicates that no detectable amount of ^{129}I was released from the nuclear facilities in Risø.

Table 2 lists the reported ^{129}I concentration and ^{129}I/^{127}I ratios in some environmental samples. Compared with our results, it can be seen that the ^{129}I levels in soil and grass analysed in this work were more than one order of magnitude lower than those collected in the vicinities of some nuclear facility, such as Sellafield, UK, Mol, Belgium and WAK reprocessing plant, Germany, and within the ranges of environmental background levels in Germany and Japan.

2.1 Pre-concentration of iodine from seawater

It was reported that solvent extraction with CCl_4 can effectively separate iodine from aqueous samples. However, the results of tracer experiments with ^{131}I show that only about 40% of iodine in seawater can be extracted. The main reason is probably the high concentrations of chlorine and bromine in seawater and similar chemical properties between Cl, Br and I. Our previous work indicated that the recovery of iodine significantly decreased with increasing concentrations of Cl^- and Br^- in extraction.[25] For the determination of ^{129}I in seawater by AMS, Zhou[8] extracted iodine from seawater with CCl_4 after adding stable iodine carrier (5–50 mg l^{-1}), but no chemical yield was reported. Our tracer experimental results indicate that the recovery of iodine increases with increasing iodine concentration in solution. When the iodine concentration was increased to 2 mg l^{-1} and 10 mg l^{-1}, the recovery of iodine reached 70% and 83%, respectively (Table 3).

In the extraction of iodine, the consumption of CCl_4 will be huge for the treatment of a large volume of sample. Considering the chemical toxicity of CCl_4 and economics, the reduction of the sample volume of seawater before extraction is necessary. In addition, for increasing the chemical recovery of iodine in extraction, a large quantity of iodine carrier has to be added for a large volume of seawater. This will interfere in the determination of ^{129}I by triple neutron capture reaction of ^{127}I and raise the Compton background by activity of ^{126}I produced by fast neutron activation of ^{127}I. It can also be partly overcome by reduction of the sample volume. It has been reported that

Table 1 Analytical results of some environmental samples for ^{129}I and ratio of ^{129}I/^{127}I

				^{129}I			^{127}I			^{129}I/^{127}I	
Sample	Sampling date	Sampling location	Weight or volume	Amount/g	Conc/g g^{-1a}	Uncert.[b] (%)	Amount/g	Conc/g $g^{-1a,c}$	Uncert.[b] (%)	Ratio	Uncert.[b] (%)
Grass	22-09-98	Roskilde	40 g	5.56×10^{-12}	1.39×10^{-13}	7.81		1.00×10^{-6}	2.71	1.39×10^{-7}	8.30
Grass	22-09-98	Roskilde	40 g	5.12×10^{-12}	1.28×10^{-13}	4.93		9.50×10^{-7}	2.84	1.35×10^{-7}	5.71
Grass	20-09-98	Valby	40 g	5.41×10^{-12}	1.35×10^{-13}	5.30		4.90×10^{-7}	2.94	2.76×10^{-7}	6.04
Grass	20-09-98	Valby	40 g	5.14×10^{-12}	1.29×10^{-13}	2.78		4.65×10^{-7}	2.10	2.77×10^{-7}	3.48
Seawater	21-09-98	Roskilde Fjord	4 l	9.95×10^{-12}	2.49×10^{-12}	3.59		3.00×10^{-5}	2.10	8.30×10^{-8}	4.15
Seawater	21-09-98	Roskilde Fjord	10 l	2.35×10^{-11}	2.35×10^{-12}	2.09		3.00×10^{-5}	2.10	7.83×10^{-8}	2.96
Seawater	01-09-98	Roskilde Fjord	5 l	1.04×10^{-11}	2.08×10^{-12}	3.69		3.00×10^{-5}	2.10	6.93×10^{-8}	4.11
Fucus ves.	06-09-88	Rujkjavik Havn	40 g	4.99×10^{-11}	1.25×10^{-12}	0.65	11.1×10^{-3}	2.77×10^{-4}	0.25	4.50×10^{-9}	0.70
Fucus ves.	14-12-89	Iceland (1)	40 g	5.21×10^{-12}	1.30×10^{-13}	6.20	13.2×10^{-3}	3.30×10^{-4}	0.22	3.95×10^{-10}	6.20
Fucus ves.	25-12-89	Iceland (2)	40 g	8.65×10^{-12}	2.16×10^{-13}	4.38	14.5×10^{-3}	3.64×10^{-4}	0.40	5.97×10^{-10}	4.39
Fucus ves.	14-04-92	Klint, Denmark	10 g	2.43×10^{-10}	2.43×10^{-11}	0.90	3.75×10^{-3}	3.75×10^{-4}	1.40	6.48×10^{-8}	1.61
Fucus ves.	13-11-89	Klint, Denmark	10 g	1.31×10^{-10}	1.31×10^{-11}	0.75	3.28×10^{-3}	3.28×10^{-4}	1.27	3.99×10^{-8}	1.48
Soil	11-01-99	Roskilde, Denmark	3.0 g	1.36×10^{-12}	4.52×10^{-13}	18.6		5.92×10^{-6}	1.74	7.63×10^{-8}	18.7
Soil	11-01-99	Roskilde, Denmark	5.0 g	2.16×10^{-12}	4.32×10^{-13}	10.2		5.92×10^{-6}	1.74	7.30×10^{-8}	18.7
Blank[d]				$< 1.7 \times 10^{-13}$			8.34×10^{-6}		15.2		
Blank[e]				$< 1.4 \times 10^{-13}$			$< 7.6 \times 10^{-6}$				
Blank[f]				$< 1.8 \times 10^{-13}$			$< 6.9 \times 10^{-6}$				
^{131}I			8.8 MBq	6.54×10^{-9}		0.13	$< 3.4 \times 10^{-5}$				
^{125}I			0.5 kBq	$< 2.0 \times 10^{-13}$			3.99×10^{-5}		6.70		

[a] The concentration unit of ^{129}I and ^{127}I in seawater is g l^{-1}. [b] Uncertainty is defined as counting uncertainties at the 95% confidence level. [c] The concentrations of ^{127}I in grass, seawater and soil were determined *via* measuring ^{128}I ($T_{1/2} = 25$ min) produced by reaction ^{127}I(n, γ)^{128}I . [d] Using 4 l deionized water instead of seawater, other chemicals and analytical procedure were the same as seawater except no KI carrier addition. [e] 120 ml of 1.0 mol l^{-1} KOH solution, other chemicals and analytical procedure were the same as seaweed except no seaweed and ^{125}I addition. [f] 10 g KOH, other chemicals and analytical procedure were the same as soil except no soil and ^{125}I tracer addition.

iodide in basic solution is quite stable on evaporation under low temperature.[26] We studied the loss of iodine in seawater under evaporation using ^{131}I tracer. The results show that with pH > 9, 94–98% of iodine (as I^- and IO_3^-) was retained in the solution after evaporation on a hotplate with boiling and with more than 20-fold concentration of seawater. Thus, before evaporation, the pH of seawater was adjusted to more than 9.0 by KOH. The analytical results of three seawater samples indicate that the recovery of iodine in the pre-concentration procedure ranges from 56 to 62%.

In seawater, iodine occurs predominantly as dissolved iodate and iodide.[27] For extracting all iodine with CCl_4 as I_2, all chemical species of iodine were usually oxidized to IO_4^- with NaClO at pH 10, after which the IO_4^- was reduced to I_2 by $NH_2OH{\cdot}HCl$ at 2–3 mol l^{-1} of HNO_3.[8,28] It will consume a large quantity of HNO_3. Sulfurous acid or its salt is a strong reductant, and was usually used to reduce I_2 to I^- in the determination of iodine. Our tracer experimental results indicate that SO_3^{2-} can also rapidly and completely reduce IO_3^- to I^- under acidic media (pH < 6). Thus, in this work, all chemical species of iodine in seawater were firstly converted to I^- with $KHSO_3$ at pH 1.0, after which the I^- was then oxidized to I_2 by $NaNO_2$ for extraction to the CCl_4 phase.

2.2 Separation of iodine from vegetation and soil samples

A combustion method is widely used for the separation of iodine from vegetation and soil samples, in which the sample is placed in a quartz tube and heated to 1000–1100 °C under a stream of oxygen, and the released iodine is trapped by activated charcoal or an alkaline solution.[14–16,18,19,29–31] However, for large amounts of vegetation samples, it is not very suitable because of production of a lot of CO_2, which makes the complete retention of released iodine by alkaline solution more difficult. If activated charcoal is used to trap the released iodine and analysed directly by irradiation with neutrons, the impurities in charcoal, such as U, I, Cs, Te and Br, will probably interfere in the determination of ^{129}I.

It has been reported that iodine can be easily separated from seaweed, such as kombu (*Laminaria japonica*), by leaching with deionized water and directly extracted by CCl_4 from the leachate.[32] This is based on the fact that most of the iodine in seaweed can be leached by water and a large part of iodine exists as inorganic iodine (I^- and IO_3^-) in the leachate. However, our previous work indicated that, with the exception of a few species of seaweed, such as *Laminara japonica*, in most species of seaweed, more than half of the iodine cannot be leached by water, and the leached iodine exists in both organic and inorganic forms.[33–35] Even for *Laminaria japonica*, we failed to separate iodine from water leachate by direct extraction with CCl_4 because of difficulties in isolation of the CCl_4 phase from the aqueous phase. This probably resulted from high concentrations of organic substances in the leachate, such as alginic acid and its salts.

Alkaline ashing followed by extraction or ion-exchange separation of iodine has also been reported for the pre-separation of iodine from vegetation samples.[36,37] It is easy to

Table 2 Comparison of ^{129}I level in some environmental samples

Sample	Location of collection	Distance from source/km	Possible releasing source	Date collected	Conc. of ^{129}I/ mBq kg^{-1}	Ratio of $^{129}I/^{127}I$	Ref.
Soil	West Cumbria, UK	< 10	Sellafield	1983	280–1700		20
Soil	Mol, Belgium	0–5	Mol	June 1983	30–198	2.7×10^{-6}–2.0×10^{-5}	15
Soil	WAK, Germany	1	WAK	1980	55.5		24
Soil	WAK, Germany	23.5	WAK		2.0	2.2×10^{-7}	23
Soil	Upper Palatinate	Environment	Fallout	1987	0.133–1.26	1.52–66.1 $\times 10^{-8}$	38
Soil	Japan	1–35	Reprocessing plant	1987	0.3–30	0.3–14 $\times 10^{-7}$	21
Soil	Krasnaya Gora, Russia	220	Chernobyl	Sept. 1991	9	9×10^{-7}	16
Soil	Mirny, Russia	200	Chernobyl	Sept. 1991	23	1.3×10^{-6}	16
Soil	Ibaraki, Japan	Environment	Fallout	1985	11–41	0.66–3.2 $\times 10^{-7}$	18
Soil	Tokaimura, Japan	Environment	Fallout		0.8–13	0.1–3.0 $\times 10^{-7}$	19
Soil (IAEA-375)	Russia	Environment	Fallout	1990	1.7	1.72×10^{-7}	19
Silage	West Cumbria, UK	< 10	Sellafield	1983	170–280		20
Vegetation	Mol, Belgium	0–5	Mol	June 1983	12–94	1.2–3.9 $\times 10^{-6}$	15
Vegetation	Upper Palatinate	Environment	Fallout	1987	0.11–14.7	0.13–8.47 $\times 10^{-7}$	38
Pine needles	Tokaimura, Japan	Environment	Fallout		< 0.8–30	$< 5 \times 10^{-8}$–2×10^{-5}	18
Heather	Gavle, Sweden	Environment	Fallout	1988	5.6	3.5×10^{-7}	16
Seaweed	Iceland			1991		2.4–3.9 $\times 10^{-10}$	7
Seawater	Kattegat			1992		3.26–6.2 $\times 10^{-8}$	8
Seaweed	Iceland			1989		3.95–5.97 $\times 10^{-10}$	This work
Seaweed	Klint, Kattegat			1989–1992		3.99–6.48 $\times 10^{-8}$	This work
Seawater	Roskilde Fjord			1998		6.9–8.3 $\times 10^{-8}$	This work
Soil	Roskilde, Denmark			1999	2.9	7.45×10^{-8}	This work
Grass	Denmark			1989	0.84–0.91	1.37–2.77 $\times 10^{-7}$	This work

Table 3 Recovery of iodine in seawater in extraction procedure

Concentration fold of seawater	Concentration of iodine added/mg l^{-1}	Recovery of iodine in extraction (%)		Loss of iodine in back-extraction (%)	Total recovery of iodine (%)
		First extraction	Second extraction		
1	0	37.2 ± 3.4	4.6 ± 1.8	0.6 ± 0.3	41.2 ± 3.2
1	2.0	62.2 ± 3.9	6.7 ± 1.8	0.4 ± 0.4	69.5 ± 4.7
1	10.0	78.2 ± 3.1	5.9 ± 3.2	0.6 ± 0.3	83.2 ± 4.8
10	0	26.4 ± 4.2	3.6 ± 1.2	0.5 ± 0.3	28.3 ± 3.9
10	2.0	53.8 ± 2.6	5.9 ± 3.2	0.4 ± 0.3	60.2 ± 5.6
10	5.0	61.1 ± 3.8	5.3 ± 4.3	0.4 ± 0.3	65.2 ± 3.8
10	10.0	66.8 ± 3.8	6.1 ± 3.9	0.5 ± 0.3	72.7 ± 3.9
10	20.0	79.6 ± 2.4	5.5 ± 2.9	0.5 ± 0.4	84.1 ± 2.4
Fresh water	0	96.4 ± 1.8	3.2 ± 1.4	0.2 ± 0.2	99.1 ± 2.4

operate and can avoid the above problems. Thus, in this work, alkaline ashing or alkaline fusion followed by leaching with hot water and extraction with CCl_4 was used for decomposition of the sample and separation of iodine from grass, seaweed and a small amount of soil (less than 5 g). Our previous work indicated that the recovery of iodine in biological samples in alkaline ashing was influenced by ashing temperature and the quality of alkali added. Under optimum conditions of 650 °C for ashing temperature and a 0.2–0.3 weight ratio of KOH to sample, 70–85% of iodine can be recovered in the leachate.[26] In this work, a recovery as high as 98% was observed for seaweed samples; it probably resulted from the high iodine concentration (more than 100 $\mu g\ g^{-1}$) in seaweed. The total recovery of iodine, including extraction, ranges from 60 to 65% for grass samples and 85 to 97.5% for seaweed samples.

For soil, it was found that alkaline fusion at 600 °C is high enough for the decomposition of samples. In the beginning of the acidification of the filtered leachate, a large amount of precipitate was produced, which was considered to be silica.[36] However, with the addition of acid, the precipitate can be dissolved; when the pH of the solution reaches 1.0, all precipitate formed can be completely dissolved. Thus, in this work, unfiltered leachate of fused soil was directly acidified with HNO_3 to pH < 1.0. Iodine was then extracted to the CCl_4 phase. The chemical yield of iodine in soil in the pre-concentration procedure ranged from 70 to 79%.

By separation with an extraction and back-extraction cycle, iodine as HI form was separated into the back-extracted aqueous phase. For long term neutron irradiation in the reactor, the sample is required to be dried and sealed in a container. Lyophilization was usually used for this purpose.[18,19,36] However, our previous work indicated that much iodide in any kind of solution was lost in lyophilization.[26] Therefore, in this work, evaporation and drying of the separated iodine solution under alkaline conditions were used, in which MgO or LiOH was added to convert HI to MgI_2 or LiI to retain an alkaline medium. The results showed that only a small amount of iodine was lost in this procedure (recovery $> 98.5\%$).

2.3 Interferences in the determination of ^{129}I and ^{127}I

In the NAA for ^{129}I and ^{127}I, the nuclear reactions $^{129}I(n, \gamma)^{130}I$ and $^{127}I(n, 2n)^{126}I$ were used. However, there are some interfering nuclear reactions. These reactions are: $^{235}U(n, f)^{129}I(n, \gamma)^{130}I$; $^{235}U(n, f)^{130}I$; $^{128}Te(n, \gamma)^{129}Te(\beta^-)^{129}I(n, \gamma)^{130}I$; $^{133}Cs(n, \alpha)^{130}I$; $^{127}I(n, \gamma)^{128}I(n, \gamma)^{129}I(n, \gamma)^{130}I$ and $^{125}I(n, \gamma)^{126}I$. These interferences have been discussed in the literature.[29,39–41] However, the levels of various interferences vary largely with the experimental conditions and separation methods. Table 4 lists the magnitude of various interferences calculated under the experimental conditions in this work. The cross sections and fission yields used in these calculations were taken from refs. 42 and 43.

The various iodine isotopes including ^{130}I can be produced by the thermal neutron fission reaction of ^{235}U. The 529 keV γ-ray of ^{133}I in most of the samples and 364 keV γ-ray of ^{131}I in some samples were found. By measuring ^{133}I, the amounts of uranium impurities in counting sources of various samples were calculated. The results indicate that the uranium contents were lower than 5×10^{-9} g for soil and 1×10^{-9} g for other samples. Thus, the ^{130}I produced by uranium is equivalent to less than 2×10^{-15} g of ^{129}I in soil and 4×10^{-16} g in other samples. In this work, the separated ^{129}I in every sample is more than 1×10^{-12} g. Therefore, the interference from uranium impurities is negligible.

Besides ^{130}I, ^{131}I can be also produced by neutron activation of natural Te. By measurement of ^{131}I and subtracting the contribution from ^{235}U, the Te content in counting sources of various samples was calculated; it is lower than 5×10^{-9} g for soil samples and 2.3×10^{-8} g for others. The maximum contribution of ^{130}I induced by Te equivalent to 10^{-14} g ^{129}I can be regarded as negligible.

The Cs concentrations in soil, seaweed and grass are generally lower than 40 $\mu g\ g^{-1}$.[33,34, 44] Thus, the interference from Cs will be less than 1% even if all Cs was recovered in the pre-concentration procedure.

The interference from the reaction of $^{127}I(3n, \gamma)^{130}I$ varies as the square of the thermal neutron flux density and increases directly with the length of the irradiation time.[39,41] In our irradiation conditions, the interference from ^{127}I was less than 2% for seaweed and 0.02% for other samples.

For the determination of chemical yield, ^{125}I was usually added as tracer; the ^{126}I induced by the reaction $^{125}I(n, \gamma)^{126}I$ seriously interferes in the determination of ^{127}I (Table 4). The experimental results (Table 1) indicate that in the experimental conditions, ^{126}I induced by 100 Bq of ^{125}I is equivalent to 8.0 μg of ^{127}I. In this work, the iodine contents separated from grass and soil ranged from 3.5 to 30 μg, and some carrier iodine was added in seawater before separation. Therefore, ^{127}I concentrations in grass, seawater and soil samples were determined by measuring ^{128}I produced by the $^{127}I(n, \gamma)^{128}I$ reaction. For seaweed, because a large amount of ^{127}I was separated (> 3 mg), the interference induced by 100 Bq of ^{125}I tracer was lower than 0.3%. Therefore, the ^{127}I concentration in seaweed was simultaneously determined with ^{129}I by measurement of ^{126}I.

Due to the high γ-ray energy of ^{131}I, some authors used it as a tracer for the determination of chemical yield.[45] However, ^{129}I can be simultaneously produced during the preparation of ^{131}I; thus, addition of ^{131}I tracer probably interferes in the determination of ^{129}I. It was reported[30,36,46] that the isotopic ratio of $^{129}I/^{131}I$ ranges from 2.6×10^{-13} to 1.8×10^{-12} g ^{129}I kBq^{-1} ^{131}I in some ^{131}I tracer solutions. Our results (Table 1) indicate that the ^{129}I concentration in the ^{131}I tracer used in this experiment is 7.6×10^{-13} g ^{129}I kBq^{-1} ^{131}I. Thus, for the sample with a low

Table 4 Nuclear interferences calculation in the determination of ^{129}I and ^{127}I ($\Phi_{th} = 4 \times 10^{13}$ n cm^{-2} s^{-1}; $\Phi_{epi} = 2 \times 10^{11}$ n cm^{-2} s^{-1}; $\Phi_f = 1 \times 10^{11}$ n cm^{-2} s^{-1}; irradiation time, 10 h; activities at the end of the irradiation are given)

Nuclear reaction	Induced activities of iodine isotopes	Amount of element required to produce ^{130}I equivalent to 10^{-12} g ^{129}I
$^{129}I(n, \gamma)^{130}I$	1.2×10^{12} Bq^{130}I/g ^{129}I	
$^{235}U(n, f)^{129}I(n, \gamma)^{130}I$ and $^{235}U(n, f)^{130}I$	4.6×10^{5} Bq^{130}I/g U	2.6 μg
$^{235}U(n, f)^{131}I$	2.6×10^{8} Bq^{131}I/g U	
$^{235}U(n, f)^{133}I$	8.2×10^{9} Bq^{133}I/g U	
$^{128}Te(n, \gamma)^{129}Te(\beta-)^{129}I(n, \gamma)^{130}I$	5.2×10^{5} Bq^{130}I/g Te	2.3 μg
$^{130}Te(n, \gamma)^{131}Te(\beta-)^{131}I$	5.6×10^{8} Bq^{131}I/g Te	
$^{133}Cs(n, \alpha)^{130}I$	6.4×10^{2} Bq^{130}I/g Cs	1.9 mg
$^{127}I(n, \gamma)^{128}I(n, \gamma)^{129}I(n, \gamma)^{130}I$	7.2 Bq^{130}I/g ^{127}I	170 mg
$^{127}I(n, 2n)^{126}I$	1.0×10^{4} Bq^{126}I/g ^{127}I	
$^{125}I(n, \gamma)^{126}I$	4.1×10^{12} Bq^{126}I/g ^{125}I (or 1 Bq^{126}I/kBq ^{125}I)	

Table 5 Detection limits of ^{129}I and ^{127}I by NAA ($\Phi = 4 \times 10^{13}$ n cm^{-2} s^{-1}; Ti = 10 h; Td = 15 h; Tc = 10 h)

Detection limit	Grass	Seawater	Seaweed	Soil
^{129}I (10^{-13} g)	2.1	1.8	3.0	2.2
^{129}I (10^{-6} Bq)	1.3	1.1	1.9	1.4
^{129}I (10^{9} atoms)	1	0.85	1.4	1.0
^{127}I (10^{-6} g)	8.4		9.8	

^{129}I concentration, addition of ^{131}I tracer will result in a serious interference. Because ^{129}I cannot be produced in the preparation of ^{125}I, ^{125}I was chosen for chemical yield determination in this work.

2.4 Reagent blank

Because numerous chemical reagents were used in the pre-irradiation separation, and the ^{129}I content in some samples was very low, the reagent blank and contamination from the laboratory environment should be considered. In this work, three blank samples were treated using the same method as that for seawater, seaweed and soil, respectively, except using deionized water instead of the sample. The results (Table 1) indicate that no ^{129}I can be detected in all three kinds of blank samples; the ^{127}I in blank samples was also lower than the detection limit.

2.5 Detection limit of ^{129}I and ^{127}I

Pre-irradiation chemical separation and post-irradiation purification of iodine can eliminate most nuclear and chemical interferences. However, the interference from some iodine isotopes, such as ^{126}I, cannot be eliminated. When the ratio of ^{129}I/^{127}I is low, or the fast neutron fraction is high in the irradiation site, the interference from the Compton background of ^{126}I will be very serious and it will make the detection limit of ^{129}I worse. For elimination of this interference and improvement of the detection limit of ^{129}I, the coincidence measurement technique and isotopic separation after irradiation were applied.[17,30,31,39] Because the flux ratio of fast to thermal neutrons in the irradiation channel in this work was very low (2.5×10^{-3}), it is beneficial for the measurement of ^{129}I. The detection limits of ^{129}I and ^{127}I in various samples calculated according to the Currie formula[47] are listed in Table 5. It can be observed that a detection limit of ^{129}I as low as 2×10^{-13} g was obtained. However, the detection limit of ^{127}I by measurement of ^{126}I was worse; this was overcome by measurement of ^{128}I, in this case, as low as 1×10^{-9} g ^{127}I can be detected.[25]

References

1 National Council on Radiation Protection and Measurements (NCRP), Iodine-129: Evaluation of releases from nuclear power generation. NCRP Report No.75, NCRP, Bethesda, MD, 1983.

2 G. M. Raisbeck, F. Yiou, Z. Q. Zhou, L. R. Kilius and P. J. Kershaw, *Radioprotection Colloq*., 1997, **32**, C2-91.

3 G. M. Raisbeck, F. Yiou, Z. Q. Zhou and L. P. Lilius, in *Environmental Radioactivity in the Arctic*, Oslo, August 21–25, 1995, ed. P. Strand and A. Cooks, pp. 109–112.

4 F. Yiou, G. M. Raisbeck, Z. Q. Zhou, L. R. Kilius and P. J. Kershaw, Improved estimates of oceanic discharges of ^{129}I from Sellafield and La Hague, Proceedings of Second International Conference on Environmental Radioactivity in the Arctic, Oslo, Norway, 1995.

5 R. R. Edwards, *Science*, 1962, **137**, 851.

6 M. H. Studier, C. Postmus Jr., J. Mech, R. R. Walters and E. N. Sloth, *J. Inorg. Nucl. Chem*., 1962, **24**, 755.

7 F. Yiou, G. M. Raisbeck, Z. Q. Zhou and L. R. Kilius, *Nucl. Instrum. Methods Phy. Res., Sect. B*, 1994, **92**, 436.

8 Z. Q. Zhou, PhD Thesis, Universite de Paris-Sud, 1995.

9 J. N. Smith, K. M. Ellis, B. Moran, L. Polyak and G. Ivanov, *Radioprotection Colloq*., 1997, **32**, C2-97.

10 H. N. Edmonds, *Tracer application of anthropogenic iodine-129 in the North Atlantic Ocean*, PhD Thesis, Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, 1997.

11 L. M. Cooper, T. M. Beasley, X. L. Zhao, C. Soto, K. L. Vinogradova and K. H. Dunton, *Mar. Biol*., 1998, **131**, 391.

12 T. Straume, A. A. Marchetti, L. R. Anspaugh, V. T. Khrouch, Y. I. Gavrilin, S. M. Shinkarev, V. V. Drozdovitch, A. V. Ulanovsky, S. V. Korneev, M. K. Brekeshev, E. S. Leonov, G. Voigt, S. V. Panchenko and V. F. Minenko, *Health Phys.*, 1996, **71**(5), 733.

13 L. VanMiddlesworth and J. Handl, *Health Phys*., 1997, **73**(4), 647.

14 J. Handl and A. Pfau, *Sci. Total Environ*., 1989, **85**, 245.

15 J. Handl, A. Pfau and F. W. Huth, *Health Phys.*, 1990, **58**(5), 609.

16 J. Handl, E. Oliver, D. Jakob and K. J. Johanson, *Health Phys.*, 1993, **65**(3), 265.

17 L. L. Oliver, R. V. Ballad and O. K. Manuel, *Health Phys.*, 1982, **42**, 425.

18 Y. Muramatsu, S. Uchida and Y. Ohmomo, *J. Radioanal. Nucl. Chem*., 1990, **138**(2), 337.

19 Y. Muramatsu and Y. Yoshida, *J. Radioanal. Nucl. Chem.*, 1995, **197**(1), 149.

20 B. T. Wilkins, Investigation of iodine-129 in the natural environment: results and implications, NRPB-R225, NRPB, Chilton, Oxfordshire, 1989.

21 R. Seki, E. Kimura, T. Takahashi and N. Ikeda, *J. Radioanal. Nucl. Chem*., 1990, **138**(1),17.

22 G. R. Doshi, S. N. Joshi and K. C. Pillai, *J. Radioanal. Nucl. Chem.*, 1991, **155**(2), 115.

23 K. Schmitz and D. C. Aumann, *J. Radioanal. Nucl. Chem.*, 1985, **198**(1), 229.

24 H. Schuttelkopf and M. Pimpl, Radioecological studies on plutonium and iodine-129 in the surrounds of the Karlsruhe Reprocessing Plant, IAEA-SM-257/100, 1982, p. 395.

25 X. L. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, S. P. Nielsen and A. Aarkrog, *Anal. Chem*., 1999, **71**(14), in the press.

26 X. L. Hou, X. Q. Feng, Q. F. Qian and C. F. Chai, *Analyst*, 1998, **123**, 2209.

27 G. T. F. Wong, *Rev. Aquat. Sci.*, 1991, **4**(1), 45.

28 J. J. Gabay, C. J. Papenello, S. Goodyear, J. C. Paly and J. M. Matuszek, *Health Phys.*, 1974, **26**, 89.

29 G. J. Lutz, H. L. Rook and R. M. Lindstorm, *J. Trace Microprobe Tech.*, 1984, **2**(1), 31.

30 D. C. Auman, *Radiochim. Acta*, 1981, **29**, 209.

31 H. Z. Rook, J. E. Suddueth and D. A. Becker, *Anal. Chem.*, 1975, **47**(9), 1557.

32 C. L. Tseng and J. H. Chao, *Appl. Radiat. Isot.*, 1996, **47**(8), 723.

33 X. L. Hou, PhD Thesis, Chinese Academy of Science, 1997.

34 X. L. Hou and X. J. Yan, *Sci. Total Environ.*, 1998, **222**, 141.

35 X. L. Hou, C. F. Chai, Q. F. Qian, X. J. Yan and X. Fan, *Sci. Total Environ.*, 1997, **204**, 215.

36 Y. Muramatsu, Y. Ohmomo and D. Christoffers, *J. Radioanal. Nucl. Chem*., 1984, **83**(2), 353.

37 S. J. Parry, B. A. Bennett, R. Benzing, A. E. Lally, C. P. Birch and M. J. Fulker, *Sci. Total Environ.*, 1995, **173–174**, 351.

38 W. I. Deitermann, J. Hauschild, E. Robens-Palavinskas and D. C. Aumann, *J. Environ. Radioact*., 1989, **10**, 79.

39 D. C. Auman, F. Buheitel, J. Hausclid, E. Robens and H. Wershofen, *J. Radioanal. Nucl. Chem.*, 1987, **109**, 261.

40 F. P. Brauer, R. S. Strebin, J. E. Fager and J. H. Kaye, *J. Radioanal. Chem.*, 1982, **72**, 501.

41 V. J. Filistovich, T. N. Nedveckaite and B. J. Styra, *J. Radioanal. Nucl. Chem.*, 1986, **97**(1), 123.

42 IAEA, Handbook on Nuclear Activation Cross Section, IAEA-156, IAEA, Vienna, 1974.

43 M. E. Meck and B. F. Rider, Compilation of fission product yields, Vallecitos Nuclear Center, NEDO-12154-1, Pleasanton, CA, 1974.

44 C. F. Chai and H. M. Zhu, *Introduction to Tracer Element Chemistry*, Chinese Atomic Energy Press, Beijing, 1994.

45 J. Handl and W. Kuhn, *J. Radioanal. Chem.*, 1980, **56**, 213.

46 J. H. Chao, C. L. Tseng and F. I. Chou, *Appl. Radiat. Isot.*, 1998, **49**(12), 1587.

47 L. A. Currie, *Anal. Chem.*, 1968, **40**, 586.

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